The need to Reconsider Traditional Free Volume Theory for
Polymer Electrolytes

by

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The Need To Reconsider Traditional Free Volume Theory For Polymer Electrolytes

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Abstract

Pressure-temperature-volume (PVT) data have been obtained for poly(propylene glycol) of molecular weight 1025 containing $LiCF_3SO_3$ in the mole ratio 20:1. The PVT data were used to calculate the specific volumes, $V/V_{P=0,T=296K}$, associated with the pressures and temperatures for previously published variable temperature, high-pressure electrical conductivity data. It is found that the electrical conductivity depends strongly on temperature at a constant volume. Consequently, traditional free volume theory is not consistent with the data. Finally, it is shown that the features of the electrical conductivity data can be accounted for by a recently developed generalized Vogel theory.

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1. Introduction

Free volume theory has found increasing use in the description of polymer electrolytes [1-3]. The primary reason, of course, is that it provides an easily understandable, *qualitative* explanation of many phenomena [4]. Another reason for the use of free volume theory is the increased application of the Positron Annihilation Spectroscopy (PALS) technique which provides data that are usually interpreted in terms of free volume [2,3]. In the present paper, pressure-volume-temperature (*PVT*) data are reported for 20:1 PPG:LiCF$_3$SO$_3$. The *PVT* data are used to analyze previously reported variable pressure and temperature electrical conductivity data for the same material [4,5]. Specifically, the *PVT* data are used to transform the pressure and temperatures to volume. The results show conclusively that traditional free volume theory is incapable of providing a quantitative explanation of the data for PPG:LiCF$_3$SO$_3$ and, presumably, for most phenomena governed by segmental motions. As an alternative, the data are interpreted in terms of a recently developed theory of glass-forming materials [6].

2. Experimental results and data reduction

The materials were prepared using the technique described elsewhere [4]. The *PVT* measurements were provided by DataPoint Labs, Inc. of Ithaca, NY. An empirical representation of the *PVT* data is given in the Appendix and the data and empirical representation are shown in Figure 1. The *PVT* data were used to transform electrical conductance data to electrical conductivity as follows. Defining the specific volume as

$$1 - \delta = \frac{V(T,P)}{V_{296K,P=0}} \qquad (1)$$

previously reported [4,5] conductance values, G, were transformed to electrical conductivities via

$$\sigma = \frac{Gl_o}{A_o(1-\delta)^{1/3}} \qquad (2)$$

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where l_o and A_o are the length and area of the sample, respectively, at $T=296K$ and $P=0$. The electrical conductivity is plotted vs. the specific volume in Figure 2.

3. Traditional free volume theory

One of the earliest "free volume" theories of transport phenomena in glass-forming materials is that due to Cohen and Turnbull [7]. They derive the following equation for the diffusion coefficent, D, in a liquid

$$D = ga*u \exp\left[-\frac{\gamma V*}{V_f}\right] \tag{3}$$

g is a geometrical factor, $a*$ is approximately equal to the molecular diameter, u is the average speed of the molecules, γ is a numerical factor introduced to correct for overlap of free volume (It should lie between 0.5 and 1.) and $V*$ is the critical volume just large enough to permit another molecule to jump in after the displacement. In the original paper by Cohen and Turnbull [7], the free volume, V_f, is defined by

$$V_f = \overline{V} - V_o \tag{4}$$

where $\overline{V}$ is the average volume per molecule in the liquid and V_o is the van der Waals volume of the molecule.

Using the Nernst-Einstein equation

$$\sigma = \frac{q^2 nD}{kT} \tag{5}$$

it follows that

$$\sigma = \frac{q^2 nga*u}{kT} \exp(-\gamma V*/V_f) \tag{6}$$

In these equations, n and q are the concentration and charge of the charge carriers, respectively, k is Boltzmann's constant and T is the absolute temperature.

Free volume theory in this form has been applied to polymer electrolytes by several workers [1,3,8,9]. Interestingly, this theory predicts that at a constant free volume, the conductivity should decrease weakly with increasing temperature. That is because kinetic theory

requires that u vary as $T^{1/2}$. Since the remaining terms in eq. (6) are approximately temperature independent, eq. (6) can be rewritten as

$$\sigma = \frac{C}{T^{1/2}} \exp(-\gamma V^* / V_f) \qquad (7)$$

This prediction is not supported by the data since, as seen in Figure 2, the electrical conductivity at constant specific volume increases strongly with temperature. Of course, the conclusion that eq. (7) is not supported by the data is based on the assumption that the free volume is proportional to the macroscopic volume. In fact, this is the assumption that is usually made. For example, Cohen and Turnbull write that

$$V_f = V_o \left(\exp\left[\int_{T_o}^{T} \alpha dT \right] - 1 \right) \qquad (8)$$

where α is the thermal expansion coefficient [7]. A slightly different approximation that is often made is to assume that the thermal expansion of the free volume is the difference in thermal expansion coefficients of the bulk material above and below T_g [3]. However, it is clear from the data that when the macroscopic volume is held constant, the ionic conductivity increases strongly with temperature. Consequently, if free volume varies as the macroscopic volume, as follows from the definition given in eq. (4), free volume theory is not capable of representing the constant volume electrical conductivity for a typical polymer electrolyte.

The disagreement between theory and experiment is not surprising since, as discussed by Cohen and Turnbull [7], the theory was originally developed for simple van der Waals liquids and metallic liquids. The inability of free volume theory to account for phenomena governed by segmental motions has been pointed out many times in the literature. For example, in the context of dielectric relaxation data and the dielectric relaxation time, $<\tau>$, Williams has pointed out that "while variations in $<\tau>$ with T at constant P or $<\tau>$ with P at constant T appear to be reconciled by using a simple free volume theory, the constant volume experiments reveal considerable difficulties with this approach [10]." More recently, Mierzwa et al. have presented a plot (their Figure 12) related to Figure 2 for dielectric relaxation in poly(n-octadecyl methacrylate) [11].

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They concluded that "density is not the controlling parameter for the segmental dynamics in the melt state and this is especially true for the segmental relaxation in semicrystalline polymers."

One of the first attempts to modify free volume theory to account for the temperature variation of physical phenomena was by Macedo and Litovitz [12]. They employed the reaction-rate theory of Eyring [13] to arrive at the following equation for the shear viscosity

$$\eta = \left(\frac{RT}{E_v} \right)^{1/2} \frac{(2mkT)^{1/2}}{V^{2/3}} \exp\left[\frac{\gamma V^*}{V_f} + \frac{E_v}{kT} \right] \tag{9}$$

where R is the gas constant, E_v is the height of the potential barrier between equilibrium positions, V is a quantity roughly equal to the volume of a molecule and m is the molecular mass. Next, the Stokes-Einstein equation,

$$\eta = \frac{kT}{6\pi Dd} \tag{10}$$

where d is the molecular radius, is used. It is known that the Stokes-Einstein equation breaks down for fragile glasses near T_g [14,15]. However, the present data being analyzed do not extend to temperatures near T_g. Next, the Nernst-Einstein equation (eq. (5)) is used to obtain the following equation for the conductivity

$$\sigma = \frac{q^2 n V^{2/3}}{6\pi d (2mkT)^{1/2}} \left(\frac{E_v}{kT} \right)^{1/2} \exp\left[-\frac{\gamma V^*}{V_f} - \frac{E_v}{kT} \right] \tag{11}$$

At constant volume, eq. (11) can be rewritten as

$$\sigma = \frac{B}{T} \exp\left[-\frac{E_v}{kT} \right] \exp\left[-\frac{\gamma V^*}{V_f} \right] \tag{12}$$

Because of the temperature dependence in the first exponential term, this equation can account for a strong increase of the conductivity at constant volume and was used by Macedo and Litovitz to successfully reproduce the pressure and temperature dependence of the shear viscosity of several liquids [12]. These include several materials exhibiting VTF or WLF behavior. It is

important to keep in mind that eq. (12) can account for VTF or WLF behavior because that behavior is represented by the free volume factor.

In order to test eq. (12) using the data for PPG:LiCF$_3$SO$_3$, Arrhenius plots of the conductivity times the absolute temperature (log(σT) vs. 1000/T) were made at constant specific volume. Those results are shown in Figure 3. The data are not consistent with the predictions of eq. (12) since the data should fall on a series of parallel straight lines.

That eq. (12) fails for many materials was pointed out very early by Brummer [16]. In that paper, Brummer noted that eq. (12) fails for ionic migration in solutions and liquid shear viscosity. Further, it was suggested that eq. (12) might be preserved if E_v, itself, varied with volume. It is clear from Figure 3 that for PPG:LiCF$_3$SO$_3$ not only must E_v vary with volume but it must also vary with temperature. In fact, Ferrer et al. have recently emphasized the influence of temperature on dynamical properties at constant volume in various materials [17]. Specifically, plots similar to Figure 3 are shown by Ferrer et al. for the shear viscosities of triphenyl phosphite and glycerol. (The plots by Ferrer et al. use density rather than specific volume.) Consequently, based on the results shown in Figure 3, it would be difficult to modify traditional free volume theory in a meaningful way in order to account for the pressure, temperature and volume variation of the conductivity of PPG:LiCF$_3$SO$_3$.

Of course, the above treatment assumes that the free volume varies as the bulk volume. The disagreement between theory and experiment could be removed if the temperature dependence of the free volume were not the same as that for the bulk material. One way to achieve this is to modify eq. (4), the definition of the free volume. For example, Zallen has pointed out [18] that the free volume for a given process is actually equal to the "empty" volume, V_{mt}, minus the "excluded" volume, V_{xclu} so that eq. (4) becomes

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$$V_f = V_{mt} - V_{xclu} \qquad (13)$$

where the "empty volume" can be identified with the difference between the total volume and the volume of the molecules i.e. $V_{mt} \equiv \overline{V} - V_o$. In fact, as has been discussed previously, defining the free volume by eq. (13) is one way to explain the positive curvature in the variation of the electrical conductivity that some materials exhibit [5,19], at least qualitatively.

If the free volume is defined by eq. (13), the results shown in Figure 2 can be rationalized qualitatively as follows. From the definition of "empty volume" it follows that if the specific volume is constant then V_{mt} is constant. One might then assume that V_{xclu} decreases as temperature and pressure increase together. If this is true, then V_f increases as temperature and pressure increase together. Consequently, it is possible to explain the results in Figure 2 via an increase in free volume at a constant specific (or "empty") volume. Consequently, it would appear that the "excluded" volume should be included in any quantitative treatment of the electrical conductivity in polymer electrolytes based on traditional free volume theory. To date, this has not been done. In fact, given the large number of adjustable parameters that already exist in the free volume model, it is not clear that further complexity will lead to physically meaningful results. However, an alternative approach has recently been presented [6].

4. Generalized Vogel theory

An alternative theory of glass-forming polymer electrolytes has been given that is based on the defect diffusion theory of Bendler and Shlesinger [20-22]. That model was recently extended to include the effect of pressure [6]. In that model as applied to a polymer electrolyte, an ion moves when it is encountered by a single "defect." As temperature decreases or pressure increases, the single defects cluster accounting for the decrease in conductivity that occurs when temperature decreases or pressure increases. In the case of zero pressure data, the clustering of

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defects gives rise to the well-known VTF behavior [23]. The model also leads to Arrhenius behavior if the defects repel each other and do not cluster.

In fact, the defects can be identified as regions of localized free volume. Consequently, the model might be better described as a dynamical free volume model. The predictions of the model are fundamentally different from theories such as traditional free volume or the Adam-Gibbs model [24] for the following reason. All of the models contain a characteristic temperature, T_o for free volume or Adam-Gibbs and T_c for BFS. In the case of free volume or Adam-Gibbs, however, the characteristic temperature is considered to be the "limiting" glass transition temperature, T_g. However, in the BFS model, T_g always occurs at a higher temperature or pressure than T_c. The reason is that in the model T_g is the temperature at which rigidity percolates. T_c, on the other hand, is the temperature that underlies the dynamics.

To demonstrate the applicability of the BFS theory, the electrical conductivity data for 20:1 PPG:LiCF$_3$SO$_3$ were analyzed using the following equation:

$$\sigma(P,V,T) = \frac{A_\sigma}{T(1-\delta)^{1/3}} \exp\left(-\frac{B^* T_c}{(T-T_c)^{3/2}(1-\delta)}\right) \tag{13}$$

In this equation, A_σ and B^* are constants and T_c depends upon pressure, temperature and volume. The microscopic interpretation of each of the parameters is given elsewhere [6].

Equation (13) is slightly different than was used previously [eq. (5) of ref. 6] to describe the electrical conductivity of 20:1 PPG:LiCF$_3$SO$_3$ [eq. (5) of ref. 6] and the input data are also different. The new features are as follows. First, $(1-\delta)^{1/3}$ is in the denominator of the pre-exponential rather than $1-\delta$. This accounts for other temperature dependent terms in the pre-exponential. (In the development of eq. (13), a factor of l^2 occurs in the numerator. The l is the jump distance in the diffusion equation $D = l^2/6\tau_1$. In the present work, l is assumed to follow the dimensions of the sample.) Next, $1-\delta$, as given by eq. (A-1) of the Appendix, now contains the effect of thermal expansion. This affects both the ion concentration (via the pre-exponential) and the defect-defect separation (via the exponent). In addition, the PVT data are for an actual sample of 20:1 PPG:LiCF$_3$SO$_3$ while for the previous work approximate PVT data were used.

Finally, the following new form for the pressure dependence of the critical temperature was used. This is an empirical relation that is often used [25].

$$T_c(P) = \zeta\left(1 + \frac{bP}{a}\right)^{1/b} \qquad (14)$$

The quantities a, b and ζ are constants. Equation (14) is used because it gives a more accurate representation of the data at higher pressures than does the simple polynomial approximation that was used previously. The parameters are related to previously determined parameters as follows. First, $\zeta = T_c(0)$, the critical temperature at zero pressure. Next, a is related to the first derivative of the critical temperature via

$$a = \frac{T_c(0)}{\left(\dfrac{\partial T_c}{\partial P}\right)_{P=0}} \qquad (15)$$

and b is related to the second pressure derivative via

$$b = 1 - \frac{a^2}{T_c(0)}\left(\frac{\partial^2 T_c}{\partial P^2}\right)_{P=0} \qquad (16)$$

Equation (13) was best-fit to the data in the following manner. First, the three parameters, A_σ, B^* and T_c were best-fit to the $P=0$ data using the usual non-linear least squares technique [26,27]. In the present work, non-linear least squares was used to best-fit eq. (13) to the high-pressure data. The best-fit parameters are listed in Table I. Despite all of the differences, there is good agreement between the parameters quoted [6] previously and those of the present work. In fact, each of the changes resulted in a slight improvement of the fits to the data. A detailed discussion of the resultant parameters will be given elsewhere [28].

The best-fit curves are shown in Figure 2. It is seen that the agreement between the BFS theory and the data is quite good. There is some difference at high temperature and pressure, the theory giving values of the conductivity that are slightly low. The disagreement at high temperature is not surprising since the theory should be most valid near T_g. However, the reason for the difference is under investigation.

5. Summary and conclusions

It is shown that traditional free volume theory is inadequate to simultaneously describe the variation of the electrical conductivity of a typical polymer electrolyte with volume. That includes both the original formulation of Cohen and Turnbull and later modifications that attempt to include the effect of temperature at constant volume. It is shown how free volume theory can be modified, at least qualitatively, to account for the features of the data. Finally, it is shown how a recently developed generalized Vogel theory accounts for all features of the conductivity data.

Appendix

For convenience, the PVT data were treated in the following manner. First, the specific volume vs. pressure data were best-fit using a cubic equation. The coefficients vs. temperature were then best-fit using a quadratic equation. The following equations were then used to approximate the PVT data.

$$1 - \delta = V(P,T)/V_{T=296, P=0} = d(T) + e(T)P + f(T)P^2 + g(T)P^3 \qquad \text{(A-1)}$$

where
$$d(T) = 0.82937 + 4.8474x10^{-4}T + 2.8047x10^{-7}T^2 \qquad \text{(A-2)}$$

$$e(T) = -1.3973 + 7.9364x10^{-3}T - 1.6485x10^{-5}T^2 \qquad \text{(A-3)}$$

$$f(T) = 13.456 - 8.5195x10^{-2}T + 1.4632x10^{-4}T^2 \qquad \text{(A-4)}$$

$$g(T) = -35.042 + 0.22299T - 3.6949x10^{-4}T^2 \qquad \text{(A-5)}$$

However, because of the shapes of the curves, the value of f was fixed at the value for 295K for temperatures below 295K and the value of g was fixed at the value for 308K below 308K.

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Table I. Quantities relevant to the defect diffusion model for 20:1 PPG:LiCF$_3$SO$_3$.

Log$_{10}(A_\sigma)$ (The units of A_σ is S-K/cm.)	0.79
B^*	7.6
T_c(K)	149
T_g(K)	218
Temp Range of Data (K)	218-345
rms dev ($P=0$ data)	0.011
$\left(\dfrac{\partial T_c}{\partial P}\right)_T$ (K/GPa)	102
$\left(\dfrac{\partial T_g}{\partial P}\right)_T$ (K/GPa)	(196)[a] (142, 172)[b] (192, 184)[c]
$\left(\dfrac{\partial^2 T_c}{\partial P^2}\right)_T$ (K/GPa^2)	-208
$\left(\dfrac{\partial^2 T_g}{\partial P^2}\right)_T$ (K/GPa^2)	(-390)[a] (-207.6, -342)[b] (-433, -355)[c]
rms dev (High-pressure data)	0.026

a. Determined from a graphical analysis of the data for high molecular weight ($\approx 10^6$) PPO (Parel^{TM} elastomer) shown in fig. 4 of J. J. Fontanella, M. C. Wintersgill, M. K. Smith, J. Semancik, C. G. Andeen, J. Appl. Phys. 60 (1986) 2665.
b. Results for PPG 400 from ref. 25.
c. Results for PPG 4000 from ref. 25.

Figure captions

Fig. 1. Pressure-Volume-Temperature data for 20:1 PPG:LiCF$_3$SO$_3$ provided by Datapoint Labs, Inc. The lines are the best-fit polynomials given in the Appendix.

Fig. 2. Electrical conductivity vs. specific volume for 20:1 PPG:LiCF$_3$SO$_3$. The lines are the best-fit generalized Vogel equation.

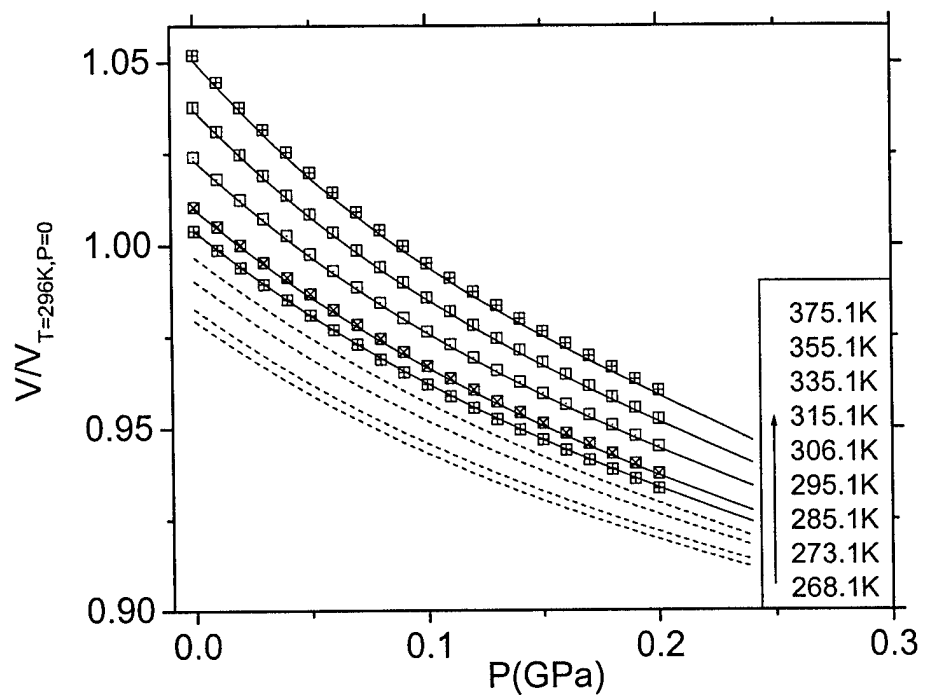**Fig. 3.** Arrhenius plot of the electrical conductivity for 20:1 PPG:LiCF$_3$SO$_3$ at various specific volumes.

Figure 1

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PPG(1025):LiCF$_3$SO$_3$ (20:1)

363K
343K
323K
308K
295K
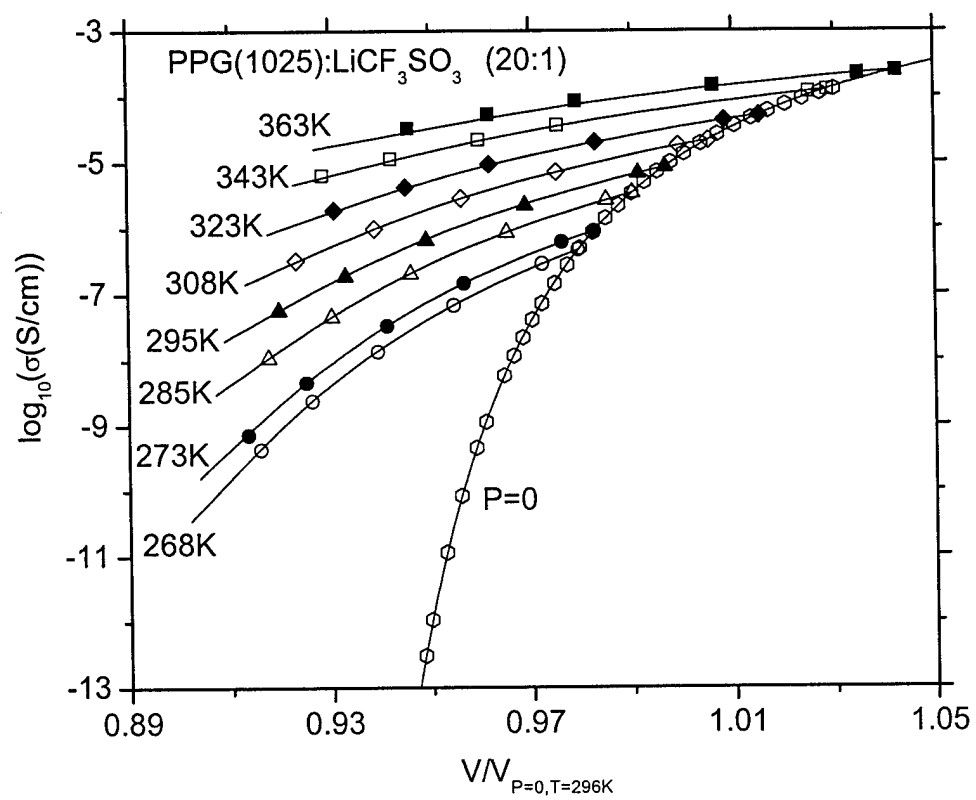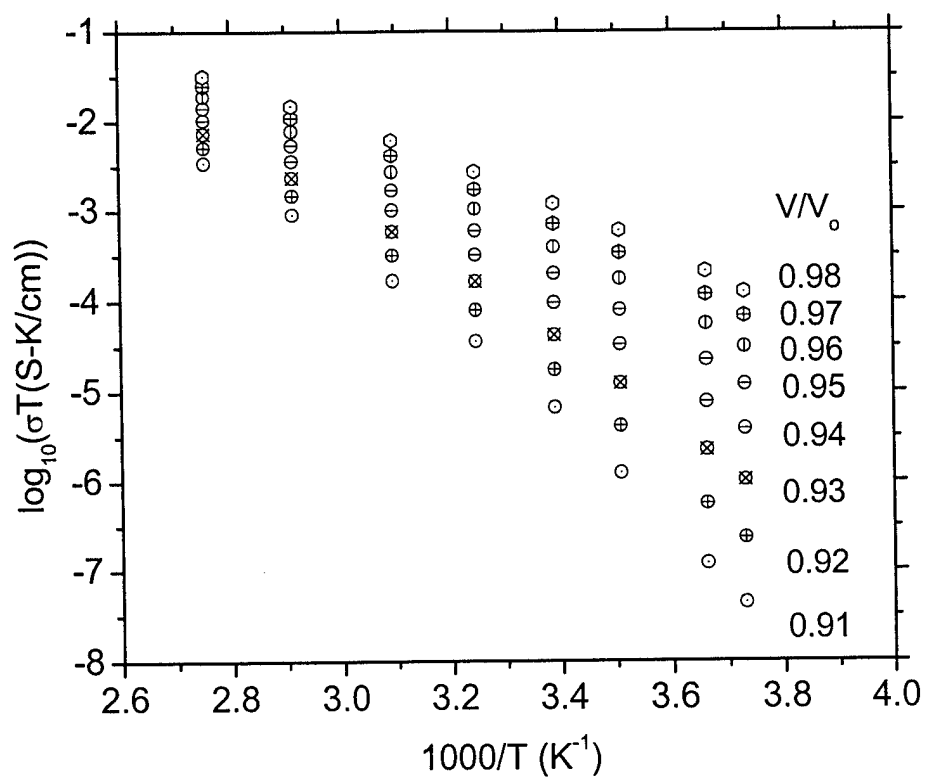285K
273K
268K

P=0

$V/V_{P=0,T=296K}$

$\log_{10}(\sigma(S/cm))$

Figure 2

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Figure 3

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